Chemical Durability of Borosilicate and Phosphate Glasses with High Content of Plutonium

L. J. Jardine, LLNL

A. S. Aloy, O. A. Iskhakova, A. V. Trofimenko
V. G. Khlopin Radium Institute, St. Petersburg, Russia

B. A. Shakhmatkin, Institute of Silicate Chemistry of the Russian Academy of Sciences
C. St. Petersburg

Lawrence
Livermore
National
Laboratory

DISCLAIMER

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

This is a preprint of a paper intended for publication in a journal or proceedings. Since changes may be made before publication, this preprint is made available with the understanding that it will not be cited or reproduced without the permission of the author.

CHEMICAL DURABILITY OF BOROSILICATE AND PHOSPHATE GLASSES WITH HIGH CONTENT OF PLUTONIUM.

A.S. ALOY, O.A. ISKHAKOVA, A.V. TROFIMENKO

RPA "V.G. Khlopin Radium Institute", 194021, 2nd Murinskiy prosp 28, St. Petersburg, Russia.

B.A. SHAKHMATKIN

Institute of Silicate Chemistry of the Russian Academy of Sciences, 199155, Odoevvskogo Str. 24/2, St. Petersburg, Russia

L.J. JARDINE

University of California, Lawrence Livermore National Laboratory, P.O. Box 808, L–195, Livermore, CA 94551

ABSTRACT

After the preparation of borosilicate and phosphate glasses containing 2,67 and 4,46 wt.% PuO_2, respectively, their water durability was evaluated by the standard MCC–1 static test at 25 ^{o}C and 90 ^{o}C.

The ratio of the surface area (SA) of the active glass specimen to the leachant (distilled water) volume (V) was——— SA/V= 0,1 cm^{-1}.

All of the leachants were sampled after intervals of 3, 14 and 28 days and the concentration of leached inactive elements was analyzed (ICP–AES) after plutonium was separated with resins. The leachants activity measurements ,as well as glass specimen's activity before and after leaching, were conducted using gamma spectroscopy.

The release of plutonium from phosphate glass at 90 ^{o}C is two orders of magnitude higher in comparison with borosilicate glass. The temperature influence is also greater for phosphate glass. At 90°C, the release of Pu became approximately 10 times more than at 25 ^{o}C, but the bulk components release (Si, B, P, Na) increased by two orders of magnitude.

1. Introduction

In the development of an optimal concept for disposition of fissile materials, the main criteria should include the safety and the protection of the environment from the radiological impacts. One of the possible routes could be a vitrification option, particularly if combined with high–level waste (HLW) treatment [1].

The selection of a vitrification route depends on many factors, including the uniformity of the distribution of Pu in the glasses and their chemical durability.

Basically, the latter characteristics were studied for HLW phosphate or borosilicate glasses containing a small amount of plutonium [2,3]. For example, in [2] the normalized Pu mass loss in ISO – leach test was from 0,28 g/m^2 at 25 ^{o}C up to 0,79 g/m^2 at 90 ^{o}C after 32 days. Testing of high Pu–loaded glasses that contain 2 and 7 wt.% Pu by PCT, version B, method gave the normalized release Pu $(2–4) \cdot 10^{-3}$ g/m^2 after 215 days [4].

In our work the corrosion behavior of the phosphate and borosilicate glasses containing plutonium was studied using an MCC–1 method to compare their durability in the same conditions.

2. Experimental

Based on the theoretical assessment of the thermodynamic behavior of PuO_2 in borosilicate and phosphate melts, the corresponding glass formulations for high Pu dissolution levels under appropriate process conditions, were selected.

To produce borosilicate glass ,the oxides of elements–modifiers, nitrates of Na and Cs as well as SiO_2 and H_3BO_3 were mixed and thoroughly ground with a fine powder of PuO_2. The particle size of PuO_2 in a batch did not exceed 100 micron.

The synthesis of Pu–containing phosphate glass was performed based on the preliminary melted and ground glass frit of a calculated composition Then this premelted glass frit was mixed with fine PuO_2 powder.

In both glass types Gd was added as neutron absorber.

Both glasses with Pu were melted in an alumina crucible using a resistance furnace placed in glove–box. After 2 hours exposure at 1150 ^{o}C for borosilicate and 1100 ^{o}C for phosphate compositions, the melts were poured into stainless–steel forms and annealed.

According to X–ray and SEM analysis, the glasses were fully amorphous and homogeneous.

Their compositions, as well as specific activities and the content of PuO_2 dissolved in glass, were determined by gamma–spectrometry. The results are shown in the Tables 1 and 2.

Table 1.

Borosilicate glass composition containing Pu. (BS-5)

Component	SiO_2	B_2O_3	Na_2O	Al_2O_3	Cs_2O	ZnO	BaO	Fe_2O_3	Gd_2O_3	PuO_2
Concentration (wt.%)	42.50	16.90	20.50	2.05	2.05	5.10	4.10	3.10	1.03	2.67
Specific activity = $(5,46\pm0,3) \cdot 10^4$ (Bq/mg)										

Table 2.

Phosphate glass composition containing Pu. (PH-5)

Component	P_2O_5	Na_2O	Al_2O_3	Cs_2O	ZnO	BaO	Fe_2O_3	Gd_2O_3	PuO_2
Concentration(wt.%)	60.30	10.05	8.05	3.02	4.04	3.02	2.01	5.05	4.46
Specific activity = $(9,18\pm0,3) \cdot 10^4$ (Bq/mg)									

The leaching of Pu and other main glass components was evaluated by MCC–1 static tests at 25 and 90 ^{o}C with a SA/V = 0,1 m^{-1}. [5]

After each sampling, the capsule walls were treated by 6M HNO_3 solution with H_2O_2 at 70 ^{o}C for 24 hours and the resulted solutions were combined with the leachants to measure the total Pu activity.

The concentration of leached inactive elements were analyzed by IPC–AES method after separation of Pu from the solutions with resins.

The leachants activity measurements, as well as glass specimens before and after thee tests, were conducted using gamma–spectroscopy.

Normalized elemental mass losses (NL_i) were calculated by the following equation:

$$NL_i = \frac{A_i}{n_i} ? \frac{1}{SA}$$; where NL_i is the normalized mass loss (g/m^2) for element i, A_i is the mass loss (g) of

the element i, based on its concentration in the leachante, n_i is the mass fraction of element i in the waste form, ⸺SA is the surface area (m^2) of the waste form exposed to the leachante.

3. Results and discussion.

The results of the MCC-1 tests on the glasses are shown in the Tables 3 and 4, as well as in Figures 1 and 2, graphically.

These data indicate that the corrosion rate of PH-5 glass is faster in comparison with BS-5. The temperature influence on the total dissolution rate is also greater for PH-5. At 90C, the release of Pu and Gd became only 10 times more approximately from PH-5 than BS-5, while the bulk components release (Si, B, P, Na) increased by two order of magnitude.

In comparing the results of Pu and Gd releases from these tests, it should be noted that Pu is released more rapidly but their behavior is very similar. An important aspect of the safety is the specific behavior of the Pu and neutron absorbers. At high temperature boron is released very rapidly from BS-5, while the Pu and Gd are released at a much lower rate. Note that Gd is more effective neutron absorber.

——————Table 3

Normalize loss mass phosphate glasses (g/m^2)

Type	T (C^o)	Days	Element				
			Na	P	Al	Gd	Pu
PH–5	90	3	58.28	24.81	9.23	0.1209	0.9429
		14	79.81	69.34	19.31	0.3135	1.8937
		28	179.12	149.79	30.03	0.5311	1.9789
	25	3	0.60	0.59	0.03	0.0228	0.0075
		14	0.78	0.78	0.06	0.0576	0.0214
		28	1.49	1.51	0.06	0.0778	0.0272

Table 4

Normalize loss mass for borosilicate glasses (g/m^2·)

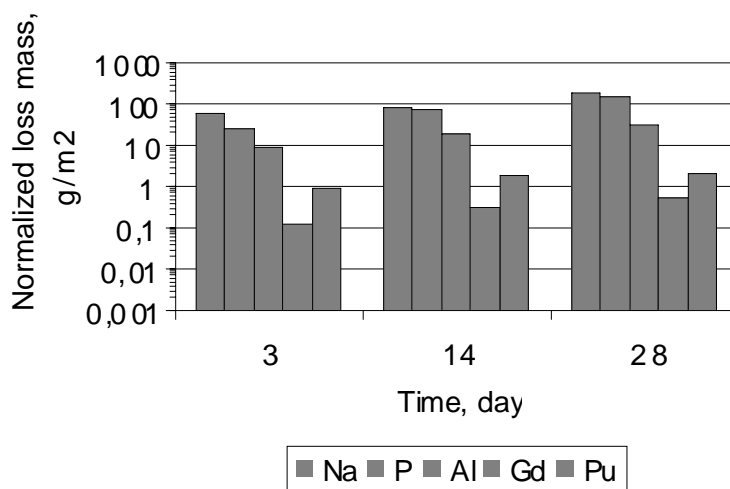| Type	T (C^o)	Days	Element				
			Na	B	Si	Gd	Pu
BS–5	90	3	22.02	18.69	12.63	0.0833	0.1105
		14	95.90	80.78	32.90	0.1308	0.5306
		28	105.92	122.14	48.79	0.1991	0.8714
	25	3	0.28	0.15	0.10	0.0451	0.0182
		14	0.73	0.49	0.39	0.0480	0.0681
		28	1.01	1.03	0.44	0.0521	0.0752

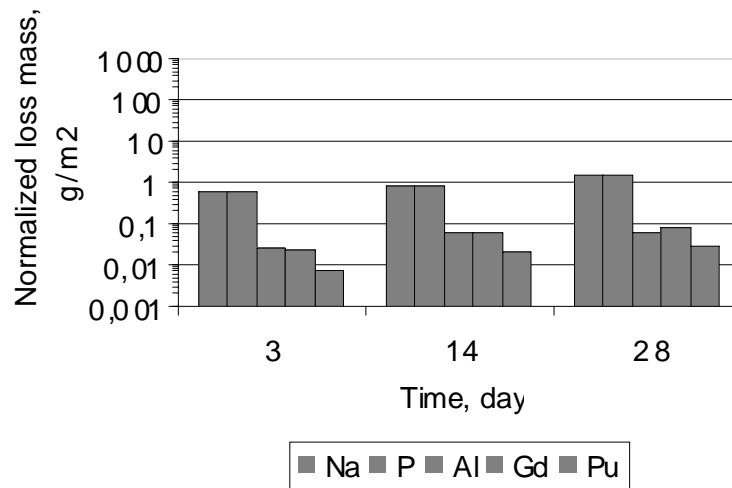Fig. 1. Normalized loss mass for phosphate glass (90 ^{o}C)

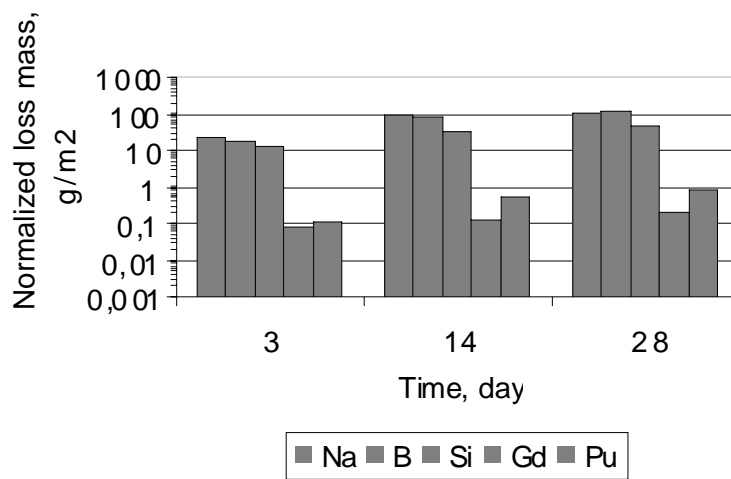Fig. 2. Normalized loss mass for phosphate glass (25 °C)

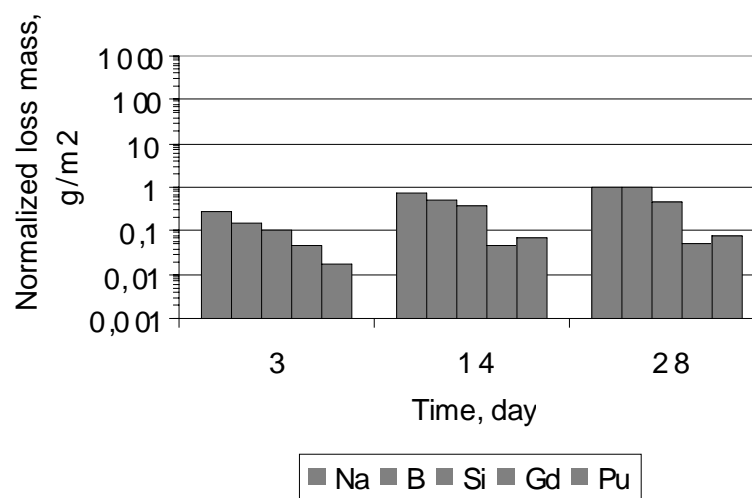Fig. 3. Normalized loss mass for borosilicate glass (90 °C)

Fig. 4. Normalized loss mass for borosilicate glass (25 °C)

Recalculated (NL_i) amounts in a number of moles reflect the incongruent nature of the dissolution process for both glasses. It means that dissolution rate is controlled by hydrated gel-layers where precipitation or adsorption of Pu and Gd takes place.

Preliminary testing of glasses with different components to accommodate high loading of Pu show that BS-5 performance is better than phosphate PH-5.

From the point of thermodynamic models, the interaction of the glass with water can be expressed as "free energy of hydration" of the different mineral formations producing the glass structure [6].

A presentation of the BS-5 composition as a set of the metasilicates, according to [6], gives the following values of the Gibbs free energy of hydration, $\_G_{hydr}$, and the Gibbs free energy of mixing, $\_G^{mix}$:

$\_G_{hydr}$ = -11.333 kcal/mol $\_G^{mix}$ = -20.411 kcal/mol

Based on the known correlation, the above value of $\_G_{hydr}$ corresponds to the value of the normalized mass loss that falls in the range of 200-10000 g/m^2 .This value exceeds the available experimental data by several orders of magnitude. However, this is being determined on the basis of minimization of the Gibbs free energy of the system and provided that all chemical processes that proceed in the system are taken into account. as was described in [7]. The actual set of species comprising the composition in BS-5 probably includes the following constituents (indicated in numbers of moles): $Cs_2O\cdot5B_2O_3$ – 0.00727, $Na_2O\cdot4B_2O_3$ – 0.0516, $Na_2O\cdot Al_2O_3\cdot4SiO_2$ – 0.02011, $Na_2O\cdot2BaO\cdot2SiO_2$ – 0.01337, $Na_2O\cdot Fe_2O_3\cdot4SiO_2$ – 0.03883, $Na_2O\cdot2SiO_2$ – 0.21369 and $2ZnO\cdot SiO_2$ – 0.01746. Taking into account the formation of the above species leads to the value of $\_G^{mix}$ equal to -30.281 kcal/mol and, hence, to a corrected value of $\_G_{hydr}$ equal to -1.463 kcal/mol. Then, in accordance with the above-mentioned correlation, the normalized mass loss, on the 28th day of leaching, are expected to be as follows:

SiO_2 – 1.668 g/m^2, B_2O_3 – 1.193 g/m^2 and Na_2O – 2.004 g/m^2. Thus, the improved model calculations coincide, in the order of magnitude, with the relevant experimental value.

4. Acknowledgements.

5. References

1. J.A.C. Marples. Proceedings of the NATO Advanced Reseach Workshop on Disposal of Weapon Plutonium – Approaches and Prospects. St. Petersburg, Russia, May 14–17, 1995, p.179–195.
2. T. Banba, K. Nukaga, T. Sagawa. J. Nucl. Sci. Technol. Vol. 2, #7, 1989, p. 705–711
3. V.V. Kushnikov, Yu. I. Matyunin, T.V. Smelova, A.V. Demin. Materials Research Society Symposium Proceedings. Scientific Basis for Nuclear Waste Management XX. Vol. 465, Boston, Massachusetts, USA, December 2–6, 1996. P. 55–64.
4. J. Bates, D.Strachan, A. Ellison,B.P. McGrail, B. Grambow, etal. Plutonium Stabilization and Immobilization, Workshop, CONF– 951259--, Washington D.C., USA, December 12–14, 1995. P. 375–388.
5. Characterization of Radioactive Waste Forms and Packages/ Technical Reports Series #383,IAEA,Vienna,1997,p.73
6. C.M. Jantzen and H.J. Plodinec. Thermodynamic model of Natural, Medieval and Nuclear waste glass durability. J. Non-Crystal Sol. 67, 207-223
7. B.A. Shakhmatkin, N.M. Vedishcheva, A.S. Aloy, M.J. Plodinec, S.L. Marra. Materials Research Society Symposium Proceedings. Scientific Basis for Nuclear Waste Management XX. Vol. 465, Boston, Massachusetts, USA, December 2–6, 1996. P. 181–187.